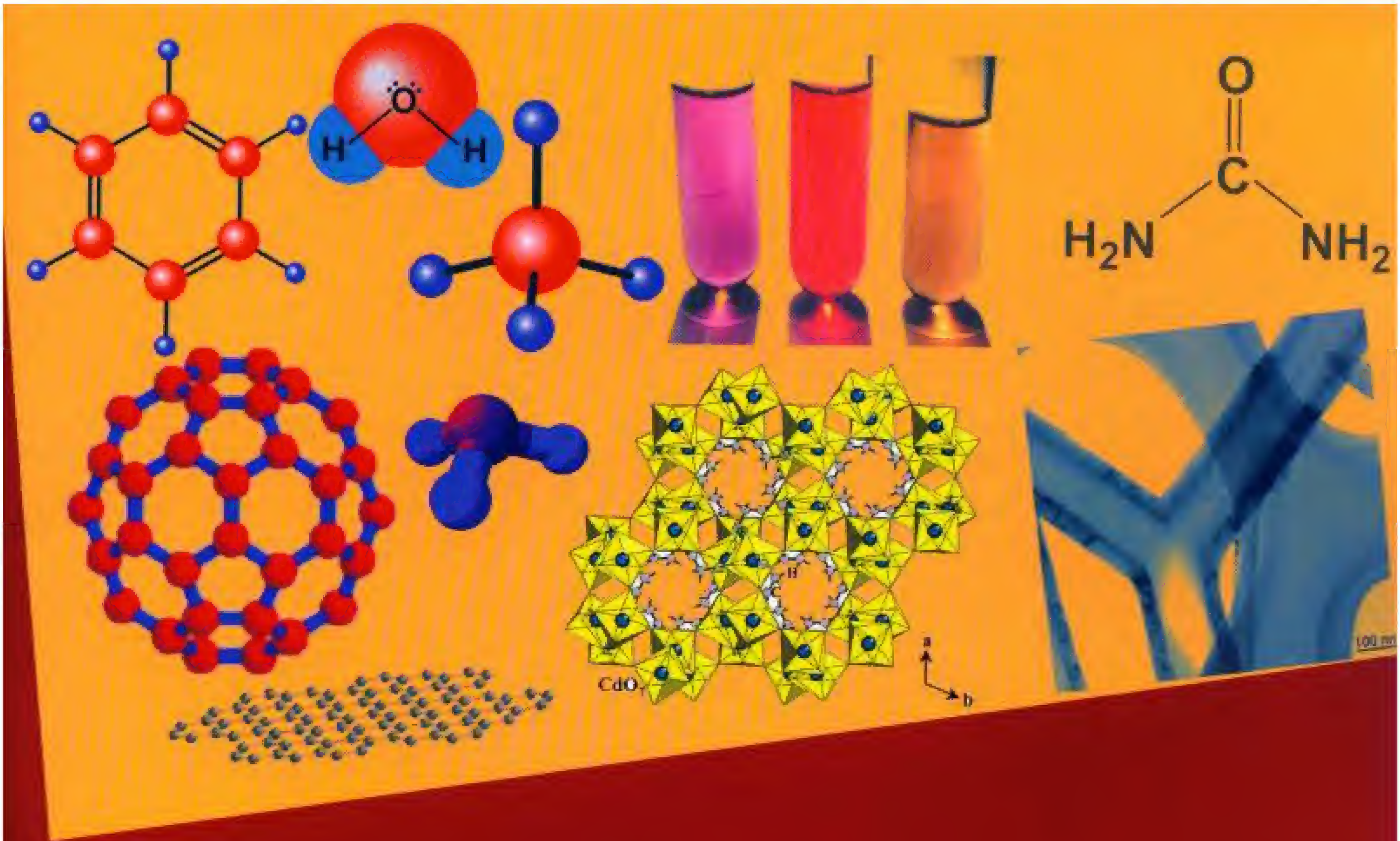

Chemistry Today

A Book to Celebrate the International Year of Chemistry

C N R RAO

CHEMISTRY TODAY

(A Book to Celebrate the International Year of Chemistry)

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Preface

Human beings started making use of chemistry several centuries ago, but the early practitioners did not know how and why things happened. Excellent chemical research was carried out during the 18^{th} and 19^{th} centuries, Lavoisier, Faraday and Dalton being prominent names from that era. The very first compound in chemistry was synthesized in 1828. Modern chemistry is, however, a 20^{th} century subject, since it is in this century that we got to know of all the elements in the periodic table. It is early in the 20^{th} century that the idea of the chemical bond was proposed. Chemistry has blossomed since then, over the last 100 years. We have many compounds and structures and we have also developed new ways of thinking about matter and life. Chemical thinking has influenced biology, materials science and other areas. The subject is growing continually and has fascinated many people. Those who have been attracted by chemistry have become worshippers of the subject. Those who have properly understood how chemistry works have become pioneers and architects of science. Good chemists generally possess a kind of intuition based on logic and creativity. This unusual attribute called chemical intuition is based on facts and theories, and contains an element which is somewhat difficult to explain to those who know little chemistry. This booklet tries to show how chemistry has progressed over the years, and highlights major developments in this extraordinary subject.

C. N. R. Rao

CHEMISTRY TODAY

CONTENTS

1.0 ABOUT CHEMISTRY

CHEMISTRY is an old science, and it is also a mother science. The chemical cornucopia is truly extraordinary.

CHEMISTRY is growing all the time.

CHEMISTRY creates new directions in science.

CHEMISTRY interacts with society continually.

CHEMISTRY serves humanity.

> *Chemists are a strange class of mortals who seek their pleasures among soot and flame, poisons and poverty, yet among all these evils, I seem to live so sweetly that I may die if I would change places with the Persian king.*
>
> \- **Becher (1625-1682)**

Let us see how chemistry has progressed in a century (1911 - 2011).

Electron was discovered in 1897.

It is only in 1911 that the structure of atoms was unraveled.

Yet, the following major developments occurred quite early.

Chemical bond (1916)

X-ray diffraction (1920)

Quantum chemistry (1930)

In 1911, we knew nothing of DNA. There were only a few chemical compounds.

Look at today! DNA is a household word.

We have millions of compounds, in the service of mankind.

2.0 SCOPE OF CHEMICAL SCIENCE

Chemical science is an old subject. Chemistry, in some form or the other, has been practiced for several centuries. In countries like India, dyes were used to make clothes attractive at least 5000 years ago. Metallurgical objects such as statues, pillars and weapons were made in many civilizations a few thousand years ago. Although we may consider the practice of chemistry as age-old, modern chemistry itself is not old. It is generally believed that chemistry, as we understand it today, started in the 18th century with Lavoisier when he propounded ideas on chemical combination, stoichiometry and combustion. We, however, knew very few elements in the 18th century. Thus, Lavoisier's periodic table had around 20 elements. It is only in the 20th century that we got to know 114 elements. If the number of elements is taken as a measure, we will have to consider chemistry to be essentially a 20th century subject. If we go to finer details, we come to recognize that new trends in chemistry started after the understanding of the nature of the chemical bond. The first attempt to understand the chemical bond was by G. N. Lewis in the early 20th century. Lewis wrote the classic paper on the chemical bond in 1916. This was followed by Linus Pauling, who wrote his famous papers and book on the nature of the chemical bond. I would, therefore, surmise that chemistry is a child of the golden age of science which occurred around 1920s. This is not surprising since X-rays were discovered during this time and quantum mechanics had its birth. The structure of atoms itself was elucidated by Rutherford not long before this period.

One of the main aspects of chemistry that has played a major role in the development of the subject relates to structure. The faith that structure forms the basis of everything in chemistry developed since the 1930s. Structure includes molecular structure, spectroscopy, chemical bonding, chemical theory and related aspects. The structural basis of chemistry as championed by Linus Pauling became the underlying theme of much of chemical research and chemical education.

I have always been surprised by the fact that it look so long for physical chemistry to be recognized as an integral part of chemistry. Ostwald and Van't Hoff were the early champions of physical chemistry, under whom most American and European physical chemists worked. Pauling was an exception and worked with Sommerfeld who trained all the well-known theoretical physicists including Heisenberg, Bethe and Born. By 1930, the leaders of physical chemistry in the US were Lewis and Pauling. It was in 1934 that the subject had its formal birth. Amazingly, the inorganic chemistry division got formally recognized by the American Chemical Society only in the 1950's. Coming back to trends and directions, the three main areas of chemistry during the 1960s and the 1970s were structure, synthesis and dynamics. Synthesis of compounds and materials is the main occupation of chemists. The first compound (urea) was made in 1828 by Wohler in Germany. Since then, there have been many advances in the synthesis of molecules and today, chemists can make almost any molecule of any complexity. There have been many great names associated with the advances in organic synthesis, Willstatter, Robinson and Woodward being the prominent ones. Progress in synthesis owes much to the development of physical techniques based on spectroscopy and diffraction. If we compare the number of compounds made before and after 1950, we really see how the number increased by several factors after the 1950s. This is almost entirely due to the availability of ready methods for quick characterization and structure elucidation.

Dynamics is an important aspect of chemistry, because it tells us how and why reactions occur. Till the middle of the 20^{th} century, one could measure rates of reaction in seconds and in the early 1960s, rates of reaction that occurred in microseconds were determined. Today, we study reactions occurring in femto seconds. The understanding of dynamics of reactions has undergone a big revolution due to better instrumentation and the development of lasers.

Ever since the advent of quantum mechanics, chemists have tried to interpret molecular structure, chemical bonding and other aspects of chemistry on the basis of quantum

mechanics. Note that the first book on quantum mechanics was by Pauling and Wilson. Even physicists read this book to learn the subject. Nowadays, most chemists use the various quantum mechanical methods routinely. Computer simulation has further strengthened the ability of chemists to explain and predict properties and behaviour of chemical systems.

Chemists have always been outgoing in research, although the teaching of chemistry may not have been always progressive. We often have to remind ourselves that molecular biology actually started in 1951 when Pauling discovered the alpha - helical structure of proteins.

To understand the way chemistry has developed, it is useful to recall the report on chemistry produced by the US National Academy of Sciences in 1985. That report mainly emphasized structure, synthesis, dynamics, catalysis and related aspects. There was a mention of materials and a little of biology, but the emphasis was mainly on molecular chemistry. Reaction dynamics got considerable importance in the report and it is not surprising that there was a vast amount of effort in this area in the subsequent period. Even funding of chemistry was influenced by this report. There was a discernible change in the late 1980s when supramolecular chemistry got recognition. Molecular chemistry was no longer considered sufficient and supramolecular approaches gained increasing importance.

Today, chemists make use of both molecular and supramolecular approaches and work on a number of interdisciplinary areas of chemical sciences. Although chemists have traditionally worked on interdisciplinary areas all through, it has become a way of life in recent years. The most important frontiers of chemistry today are related to biology and advanced materials. It is, therefore, most appropriate that the more recent report of the US National Academy of Sciences on chemistry, entitled "Beyond the Molecular Frontier", published in 2003, emphasizes less on molecular chemistry but more on materials and biology. Contributions of chemists to biology, environment, health and medicine have become so crucial that a majority of the recommendations pertain to these aspects. Similarly, synthesis and development of new materials of desired properties has come to the fore. Every few

years, a major discovery of a new molecule or a new material with unusual properties triggers chemical research in a big way. High-temperature cuprate superconductors, mesoporous silica, fullerenes and nanotubes are typical examples. Science and technology of nanomaterials have become an important pursuit of chemists in the last decade.

If I am asked to pick the greatest chemist of the 19^{th} century, I would pick Michael Faraday. Many people consider him to be a physicist, but he was a professor of chemistry. Being a professor of chemistry, he discovered electricity and carried out experiments on electrolysis, magnetism and so on. He was the first one to make nanomaterials and to experiment on the liquefaction of gases, heterogeneous catalysis and superionic conductors. He also discovered benzene.

For the 20^{th} century, Linus Pauling seems to be the obvious choice. May be it should be G. N. Lewis. If I am asked whether there will be a person who will change chemistry in a big way in the 21^{st} century, I do not have the answer. It may be difficult to find one person at the end of the 21^{st} century, because the way chemistry works today. Whatever it be, chemistry will continue to be dynamic in scope with many new frontiers to conquer in the years to come.

3.0 BEGINNING OF CHEMISTRY AND EARLY CHEMISTS

When was the beginning of Chemistry?

LAVOISIER

(Father of Chemistry)

France (1743-1794)

18^{th} Century

Conservation of mass

Composition

Air = $O_2 + N_2$

Combustion

Lavoisier was beheaded in 1794 (French Revolution).

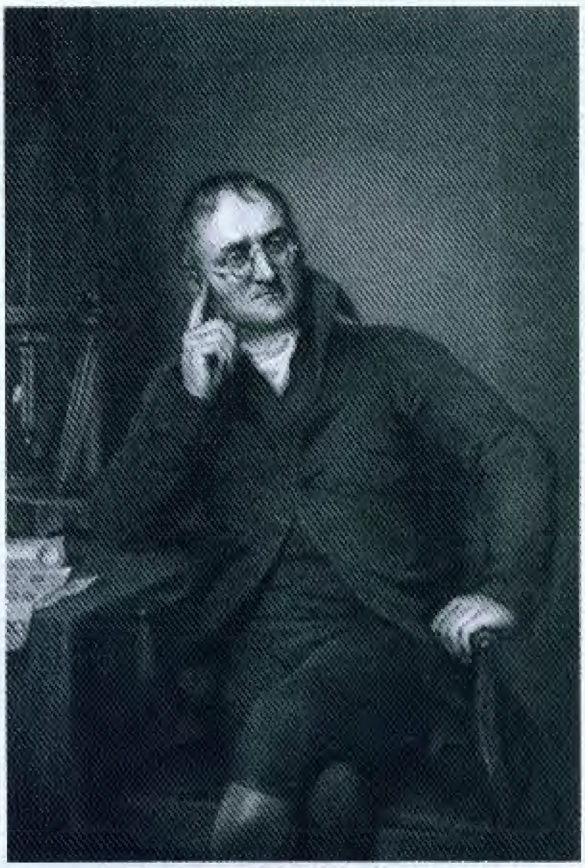
LAVOISIER (1743 - 1794)

Atomic Theory

DALTON (1803)

He also talked of proportions of elements in compounds (e.g., CO, CO_2).

Chemists were the first to believe in atoms!



DALTON (1766 - 1844)

200th anniversary of atomic theory in 2003

Dalton was a teacher of chemistry.

Some Early Chemists

1800 -1803

BERTHOLLET
Chemical reaction depends on quantity of reactants

BERTHOLLET
(1748 - 1822)

1807

HUMPHRY DAVY
Na from NaOH

HUMPHRY DAVY
(1778 - 1829)

1819 **J. J. BERZELIUS**
Electrical theory of molecules

J. J. BERZELIUS
(1779 - 1848)

1830 Isomerism in organic compounds

1858 **KEKULE**
Carbon has a valence of four

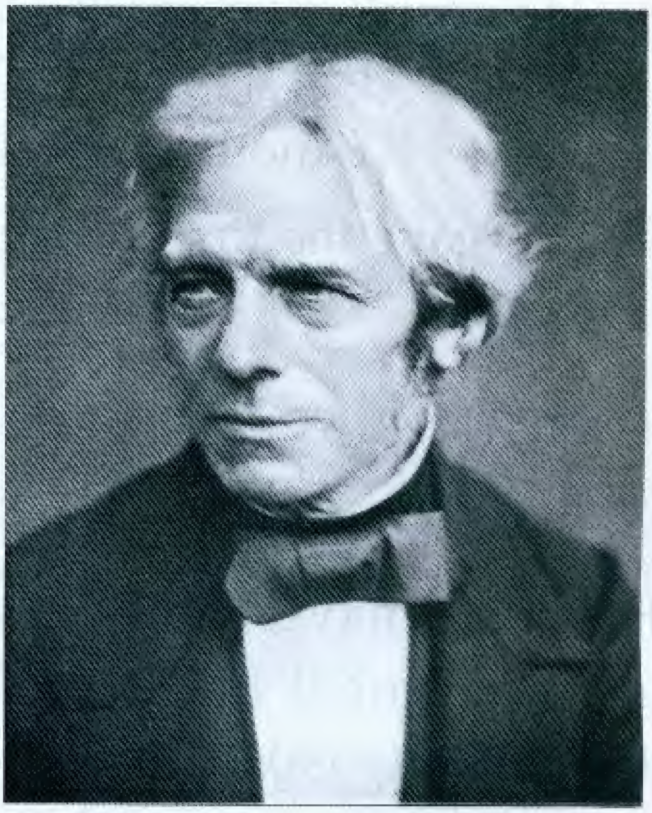
KEKULE
(1829-1896)

1874 **Le Bel and Van't HOFF**
(Carbon - Tetrahedron)
- Chemistry became three - dimensional !

Chemists used single, double and triple bonds before they understood chemical bonding.

MICHAEL FARADAY

He was a 19th century chemist.



FARADAY
(1791 - 1867)

What did Faraday do?

- Laws of electrolysis
- Liquefaction of gases
- Catalysis
- Discovery of benzene etc.
- Magnetism (Dia, Para etc.)
- Electricity
- Nanoparticles of gold
- Foundations of field theory

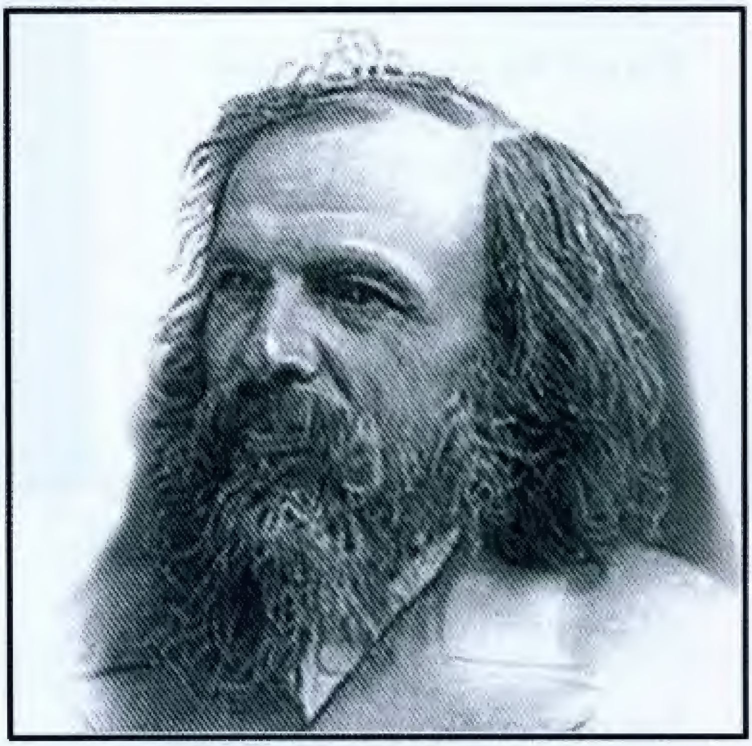
4.0 ELEMENTS AND THE PERIODIC TABLE

The great Russian Chemist DMITRI MENDELEYEV

(Another 19th century chemist.)

gave the first ideas on the periodic table.

He could have been given a Nobel Prize during 1901- 1906, but was not.



DMITRI MENDELEYEV
(1834-1907)

Chemistry is an old subject, but in one way it is a 20th century subject. We can see this from the following table.

NUMBER OF ELEMENTS

1st Century	:	7
16th Century	:	10
18th Century	:	23 (Lavoisier's table had 23 elements)
20th Century	:	114 - Today (includes Noble gases and artificial ones.)

SEABORG (1912 - 1999)
(Nobel Prize, 1951)

Seaborg and coworkers discovered plutonium and other elements.

Long form of the Periodic Table of elements recommended by IUPAC

The greatest table that man has created.

Its use will never cease!

Representative elements (Groups 1–2) · d-transition elements (Groups 3–12) · Representative elements (Groups 13–17) · Noble gases (Group 18)

period number	Group 1	Group 2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	Group 18
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
3	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
4	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
5	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^45s^1$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
6	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La*** $5d^16s^2$	72 **Hf** $4f^{14}5d^26s^2$	73 **Ta** $5d^36s^2$	74 **W** $5d^46s^2$	75 **Re** $5d^56s^2$	76 **Os** $5d^66s^2$	77 **Ir** $5d^76s^2$	78 **Pt** $5d^96s^1$	79 **Au** $5d^{10}6s^1$	80 **Hg** $5d^{10}6s^2$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
7	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac**** $6d^17s^2$	104 **Rf** $5f^{14}6d^27s^2$	105 **Db** $6d^37s^2$	106 **Sg** $6d^47s^2$	107 **Bh** $6d^57s^2$	108 **Hs** $6d^67s^2$	109 **Mt** $6d^77s^2$									

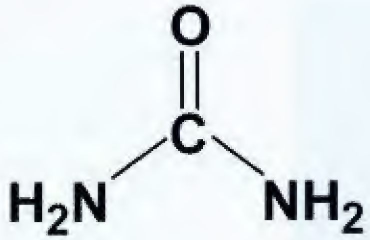
f - inner transition elements

***Lanthanides** [illegible]	58 **Ce** [illegible]	59 **Pr** [illegible]	60 **Nd** [illegible]	61 **Pm** [illegible]	62 **Sm** [illegible]	63 **Eu** [illegible]	64 **Gd** [illegible]	65 **Tb** [illegible]	66 **Dy** [illegible]	67 **Ho** [illegible]	68 **Er** [illegible]	69 **Tm** [illegible]	70 **Yb** [illegible]	71 **Lu** [illegible]
****Actinides** [illegible]	90 **Th** [illegible]	91 **Pa** [illegible]	92 **U** [illegible]	93 **Np** [illegible]	94 **Pu** [illegible]	95 **Am** [illegible]	96 **Cm** [illegible]	97 **Bk** [illegible]	98 **Cf** [illegible]	99 **Es** [illegible]	100 **Fm** [illegible]	101 **Md** [illegible]	102 **No** [illegible]	103 **Lr** [illegible]

5.0 CHEMICAL SYNTHESIS

The man who made the first compound.

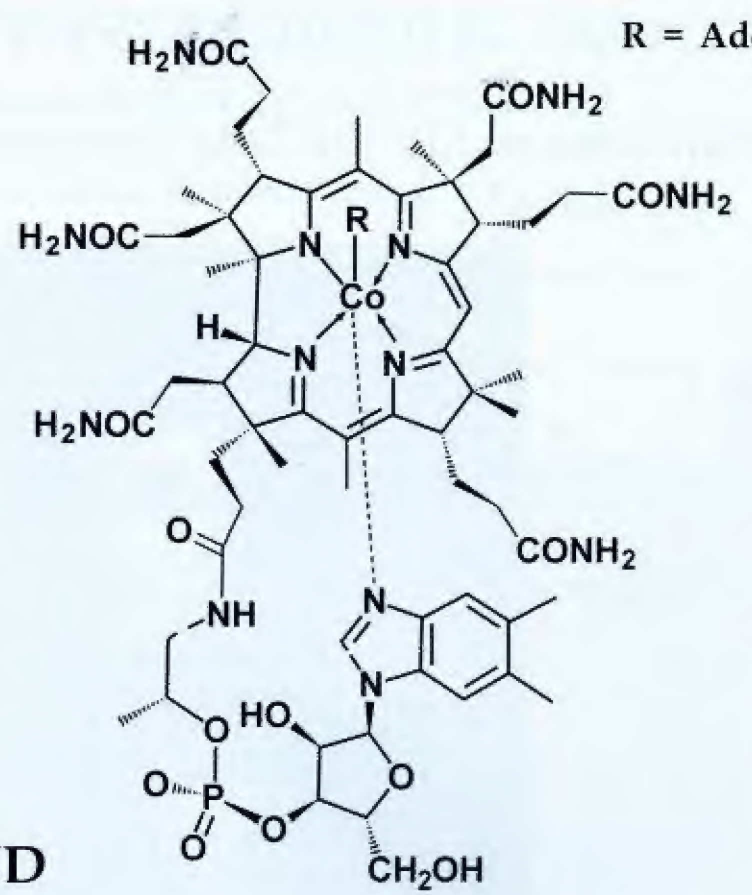
FRIEDRICH WOHLER
(1800 - 1882)



UREA

WOHLER

(1828)



FIRST COMPOUND synthesised by chemists was simple **urea.** Then they made more and more complex ones.

ESCHENMOSER & WOODWARD

VITAMIN B12

(1968)

6.0 EARLY 20th CENTURY GREATS

Organic chemists

EMIL FISCHER
(1852 - 1919)

First Nobel Prize Winner in Organic Chemistry (1902)

VICTOR GRIGNARD
(1871 - 1935)

Nobel Prize (1912)

RICHARD WILLSTATTER
(1872 - 1942)

Nobel Prize (1915)

How did Willstatter write the correct structure of cyclooctatetraene at that time?
It surprises one.

First physical chemists of the world

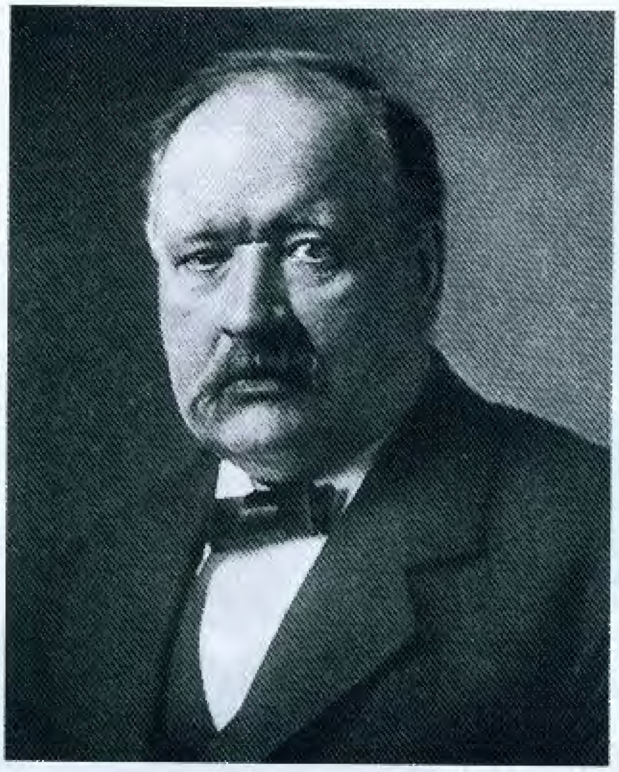
VAN'T HOFF
(1852-1911)

Nobel Prize (1901)

WILHELM OSTWALD
(1853-1932)

Nobel Prize (1909)

The other two great physical chemists of the early years



SVANTE ARRHENIUS
(1859-1927)

Nobel Prize (1903)
Electrochemistry

NERNST
(1864 - 1941)

Nobel Prize (1920)
III law, Free energy

The first famous inorganic chemists

WILLIAM RAMSAY
(1852-1916)
Noble gases
Nobel Prize (1904)

HENRI MOISSAN
(1852-1907)
Isolation of fluorine
Nobel Prize (1906)

ALFRED WERNER
(1866-1919)
Coordination chemistry
Nobel Prize (1913)

7.0 WHEN DID MODERN CHEMISTRY START?

It started when it was said that a CHEMICAL BOND is nothing but two electrons between two atoms.

$$\mathbf{A} \,\overset{\circ}{\circ}\, \mathbf{B}$$

$$\mathbf{A} - \mathbf{B}$$

$$(\text{e.g. } H - H)$$

G. N. LEWIS **(1916 paper)**

LINUS PAULING
Nature of the Chemical Bond published in 1939.
(dedicated to G. N. Lewis)

GILBERT NEWTON LEWIS

(1875 - 1946)

The chemistry department at Berkeley built by Lewis is still one of the greatest centres of chemistry.

G. N. LEWIS

(1875 - 1946)

G. N. LEWIS did not get the Nobel Prize, although he contributed more to chemistry than any other person that we know.

- The idea of the chemical bond (which is fundamental to chemistry) was his (1916). Yet, he was not recognized for this during his lifetime.
- He made thermodynamics part of chemistry and wrote the first book on the subject (Free energies of substances, correct statement of III law, activity, fugacity)
- Electrochemistry (activity, ionic strength)
- Lewis acids and bases
- Heavy Water (discovery, properties and applications)
- Early Photochemistry
- Spectroscopy (triplet state)

The name `**photon**' was coined by Lewis. Many coworkers of Lewis got Nobel Prizes (Urey, Giaque, Seaborg, Calvin).

Young Pauling with his wife.

CHEMISTRY AFTER THE CHEMICAL BOND

1930 - 1970

- Chemistry got dominated by molecular structure. Molecular conformation got recognized to be an important aspect of chemistry (Barton & Hassel, Nobel Prize 1969; Cornforth & Prelog, Nobel Prize 1975).

- New methods for the study of molecular structure came to the fore.

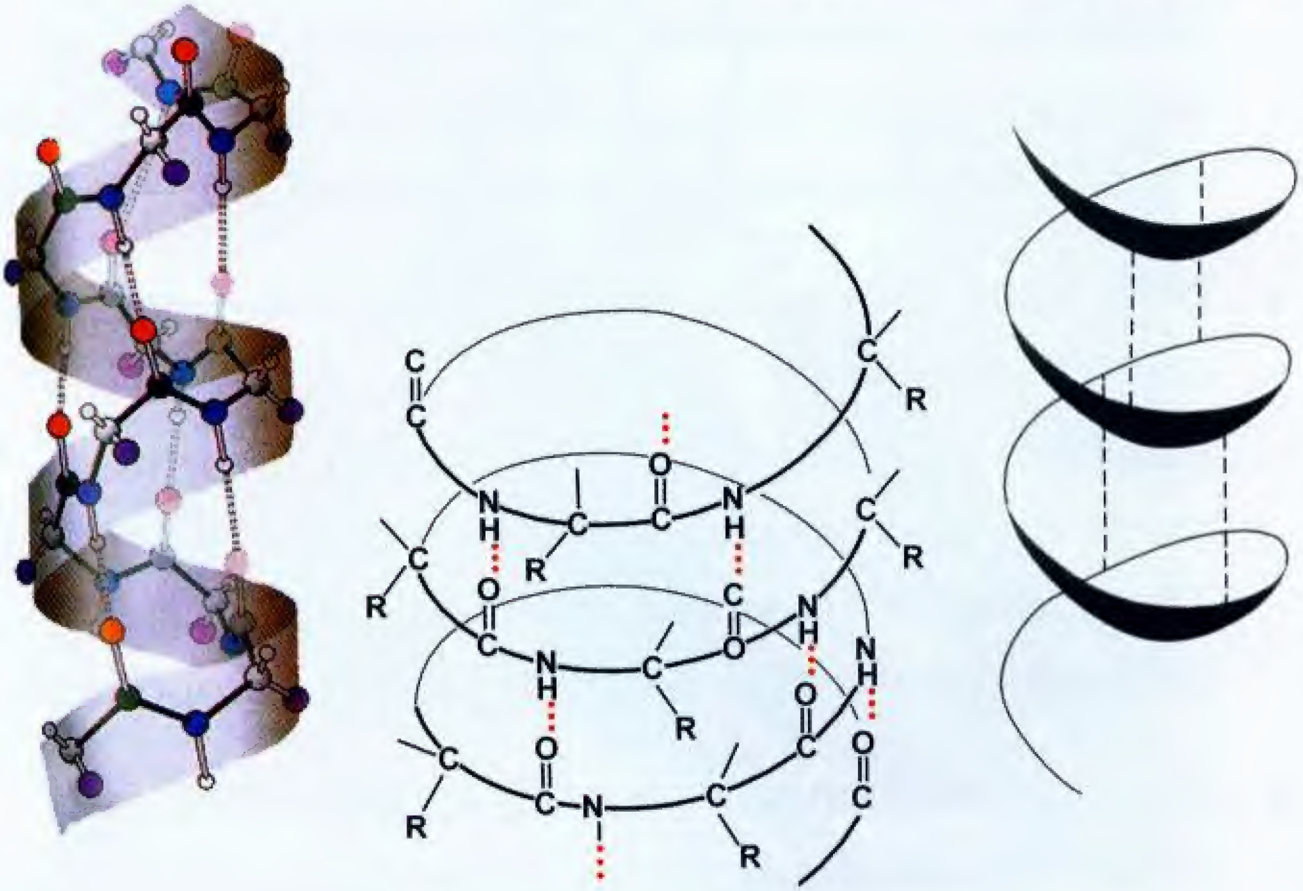
  Chemists have used spectroscopies, diffraction methods, microscopes and other means extensively. The advent of structural methods helped ease synthetic efforts and isolation of new compounds.

- Reaction mechanisms became an important area. Contributions to organic reaction mechanisms by C. K. Ingold are noteworthy.

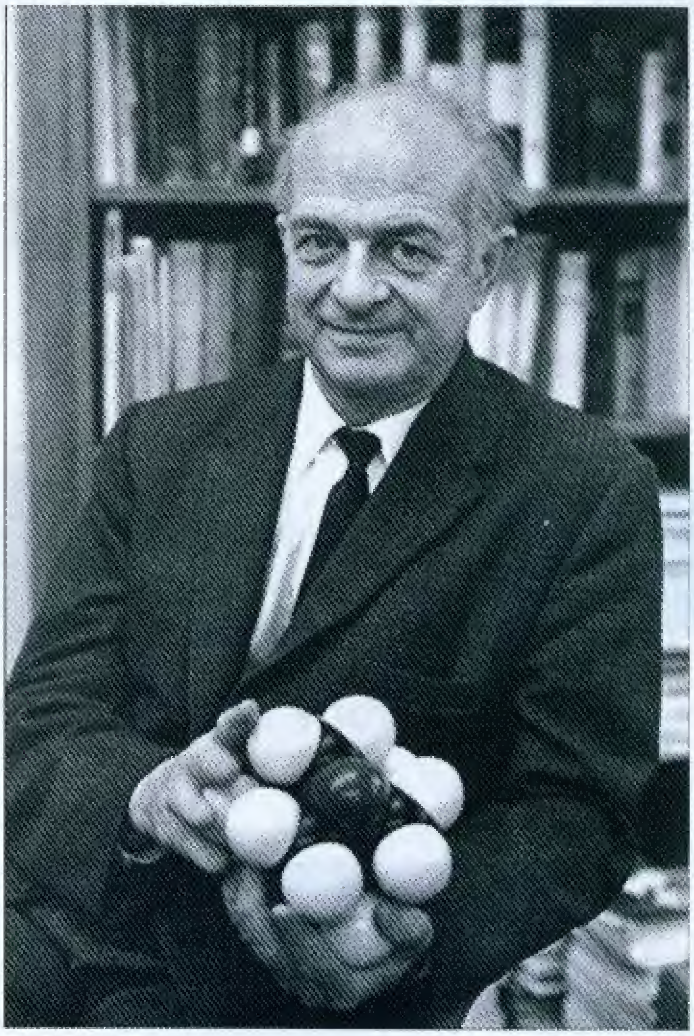
STRUCTURE OF PROTEINS

ALPHA - HELIX

LINUS PAULING (1951)



(Birth of Molecular Biology)



PAULING

Nobel Prize (1954) for chemical bonding

1960 VIEW OF CHEMISTRY

Chemistry was considered to have three major components.

STRUCTURE

SYNTHESIS

DYNAMICS

8.0 CHEMISTRY IS A CENTRAL SCIENCE

The publication of Opportunities in Chemistry in 1985 created a major change in the way the subject was viewed.

CHEMISTRY is a central science that responds to societal needs.

The report was published by
National Academy of Sciences
Washington D.C., U.S.A.

The following areas were considered to constitute INTELLECTUAL FRONTIERS IN CHEMISTRY (1985)

Chemical kinetics

Chemical theory

Catalysis

Materials

Synthesis

Life processes

Analytical methods

PRIORITY AREAS

Chemical reactivity

Chemical catalysis

Chemistry of life processes

Chemistry around us

Chemical behaviour
under extreme conditions

9.0 NOBEL LAUREATES

Synthesis and reactions

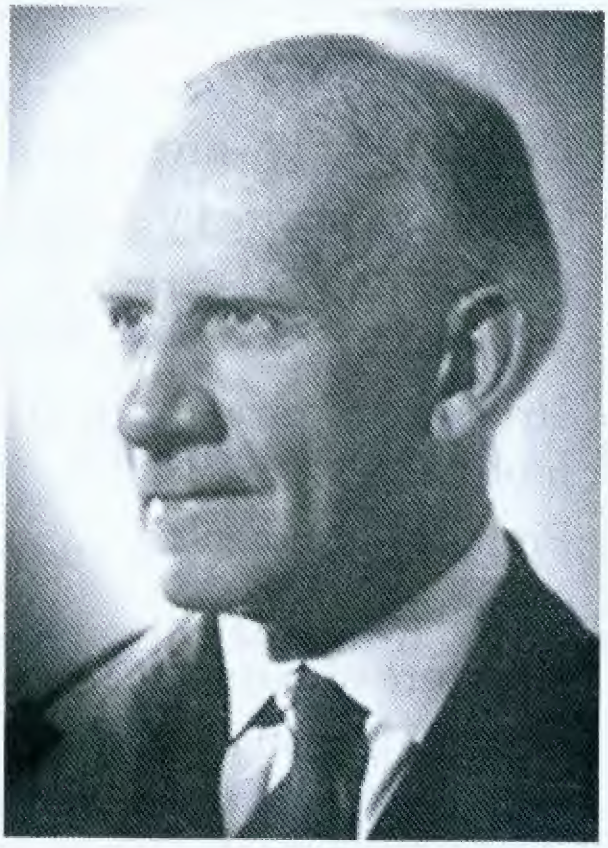
Making new compounds and discovering new reactions are two main aspects of chemistry. Although the scope of chemistry is much bigger than this, synthesis remains a major activity.

Let us look at the Nobel Prizes awarded for synthesis and chemical reactions after Willstatter (1915).

1918	Haber	Ammonia
1931	Bosch and Bergius	High Pressure chemical reactions
1937	Haworth and Karrer	Carbohydrates and carotenoids
1939	Butenandt and Ruzicka	Hormones and polymethylenes
1947	Robert Robinson	Plant products

1950	Diels and Alder	Diene synthesis
1955	du Vigneaud	Polypeptides
1957	Todd	Nucleotides
1965	Woodward	Organic synthesis
1973	Fischer and Wilkinson	Sandwich compounds
1979	Brown and Wittig	New organic synthetic reagents
1984	Merrifield	Chemical synthesis on a solid matrix
1987	Cram, Lehn and Pedersen	Supramolecular chemistry
1990	Corey	Organic synthesis
1994	Olah	Carbocations
2001	Knowles, Noyori and Sharpless	Chiral synthesis
2005	Chauvin, Grubbs and Schrock	Metathesis method in organic synthesis

Two great organic chemists of the 20^{th} century



ROBERT ROBINSON
(1886 - 1975)
Nobel Prize (1947)

R. B. WOODWARD
(1917 - 1979)
Nobel Prize (1965)

Crystallography and structure

Crystallography has been widely used in chemistry and biology to determine structures of molecules. There have been many Nobel Prizes in this area.

1914	Von Laue	Diffraction of X-rays
1915	Bragg and Bragg	Crystal structure by X-rays
1937	Davisson and Thomson	Diffraction of electrons by crystals
1954	Pauling	Structure of proteins (and molecules)
1962	Perutz and Kendrew	Proteins with X-rays
1964	Hodgkin	Structures (insulin)
1976	Lipscomb	Structure of boranes
1982	Klug	Crystallographic electron microscopy
1985	Hauptman and Karle	Direct methods in crystallography
1988	Deisenhofer, Huber and Michel	3D structure of the photosynthetic centre

Quantum mechanics

Physics Nobel Prizes

1932	Heisenberg
1933	Dirac and Schrodinger
1945	Pauli
1954	Born

Chemistry Nobel Prizes

1966	Mulliken	Molecular orbitals
1981	Fukui and Hoffmann	Frontier orbitals and chemical reactions
1998	Kohn and Pople	Methods in quantum mechanics

The first book on quantum mechanics was written by chemists (Pauling and Wilson, 1935).

Spectroscopy

Chemists have made use of spectroscopic methods extensively.

Gerhard Herzberg (Nobel Prize, 1971) made monumental contributions to infrared and Raman spectra as well as electronic spectra of molecules.

Ernst received the Nobel Prize (1991) for his contributions to high-resolution NMR spectroscopy.

Wüthrich was awarded the Nobel Prize (2002) for NMR spectroscopy of macromolecules. Fenn and Tanaka shared the 2002 prize for their work on mass spectrometry.

There are many physics Nobel Prizes as well:

Raman (1930) for Raman effect

Mössbauer (1961) for Mössbauer effect

Bloembergen and Schawlow (1981) for laser spectroscopy

Kai Siegbahn (1981) for X-ray photoelectron spectroscopy.

Chemical dynamics

In the 1950s, one measured rates of reaction occurring in minutes (and seconds rarely). Then, things changed.

Several Nobel Prizes have been awarded in this area.

1956	Hinshelwood and Semenov	(Chemical reaction kinetics)
1967	Eigen, Norrish and Porter	(High speed chemical reactions)
1986	Herschbach, Lee and Polanyi	(Dynamics of elementary reactions)
1992	Rudolph Marcus*	(Electron transfer reactions)
1995	Crutzen, Molina and Rowland	(Atmospheric reactions)
1999	Ahmed Zewail	(Femtosecond kinetics)

1967: 10^{-6} sec, 1999: 10^{-15} sec

* Henry Taube received the Nobel Prize in 1983 for his work on mechanisms of electron transfer reactions. A major slip is that Henry Eyring was not awarded a Nobel Prize.

Other areas developed to become major branches of chemistry

Polymer chemistry

Staudinger	Nobel Prize (1953)
Ziegler and Natta	Nobel Prize (1963)
Flory	Nobel Prize (1974)
Heeger, MacDiarmid and Shirakawa	Nobel Prize (2000)

Surface Chemistry

Langmuir	Nobel Prize (1932)
Ertl	Nobel Prize (2007)

10.0 SOME VETERAN INDIAN CHEMISTS

P.C. RAY
(1861-1944)

S.S. BHATNAGAR
(1884-1955)

J. C. GHOSH
(1893-1959)

T. R. SESHADRI
(1900-1975)

K. VENKATARAMAN
(1901-1981)

T. R. GOVINDACHARI
(1915-2001)

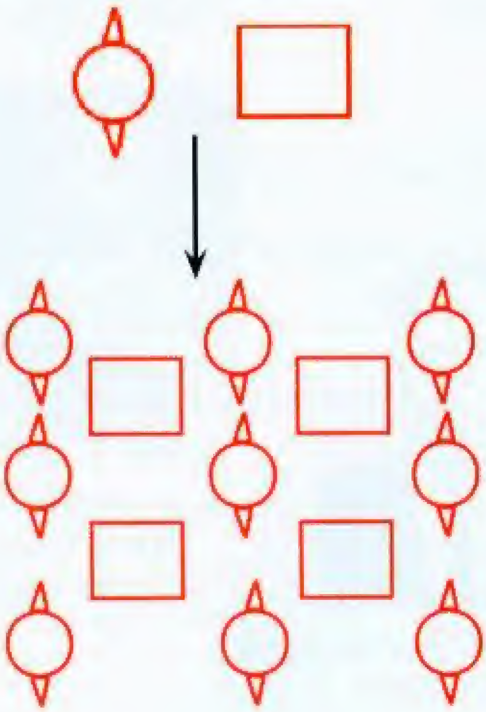
ASIMA
CHATTERJEE
(1917-2006)

11.0 SUPRAMOLECULAR BONDS

Most chemistry deals with
molecules comprising **strong covalent bonds**

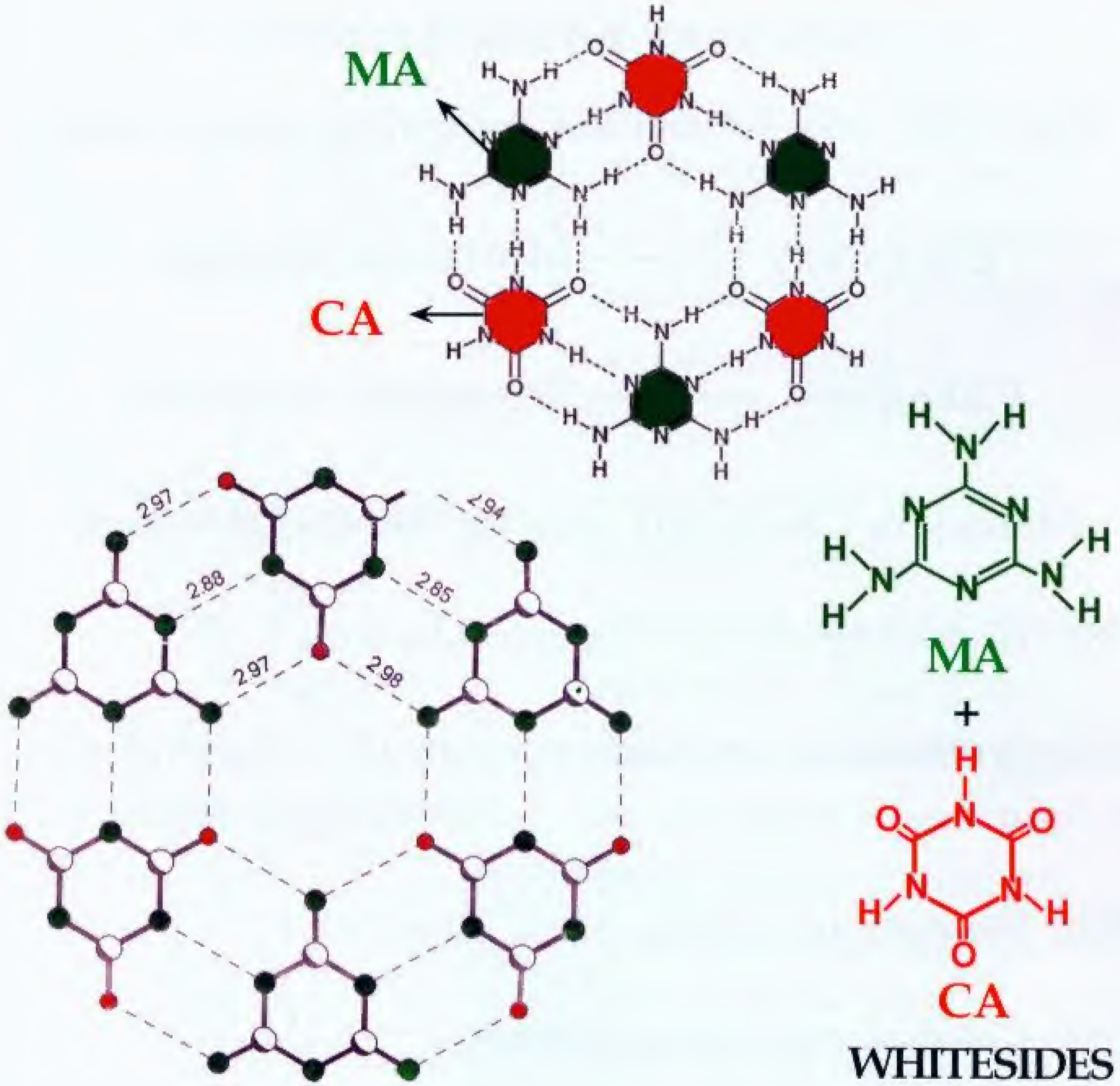
New chemistry with **weak bonds**

MOLECULAR CHEMISTRY ⟶ **SUPRAMOLECULAR CHEMISTRY**



Contains "molecular" building blocks held together by weak **noncovalent** bonds

Nobel Prize to
Cram, Lehn and Pedersen (1987)


MA
CA
2.97
2.94
2.88
2.85
2.97
2.98
MA
+
CA
WHITESIDES

12.0 NEW DIRECTIONS

Post 1980, one noticed the following interactions!

Chemistry -------- Molecular biology

Chemistry --------- Advanced materials

Materials Chemistry during the last decades:

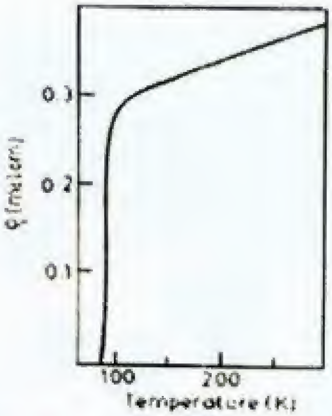
1986: High-temperature Superconductors

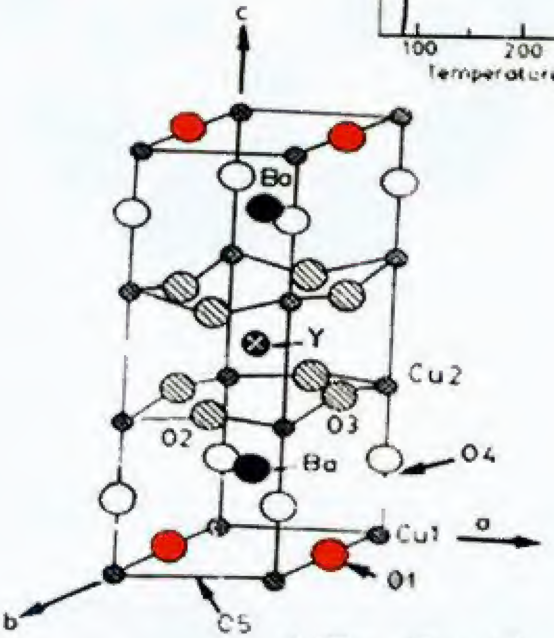
1990: Synthesis of new carbon forms (C_{60}, Nanotubes)
NANO MATERIALS

1992: Mesoporous solids

1993: Colossal magnetoresistance

High - temperature superconductors





$YBa_2Cu_3O_7$

↓

Ln

In December 1986, an oxide of copper was found to become superconducting around 35K. Till then 23K was the highest T_c. *

First liquid nitrogen superconductor (90K) in February 1987.

Superconductors became chemicals after 1987, and solid state chemistry got to be recognised as part of main-stream chemistry.

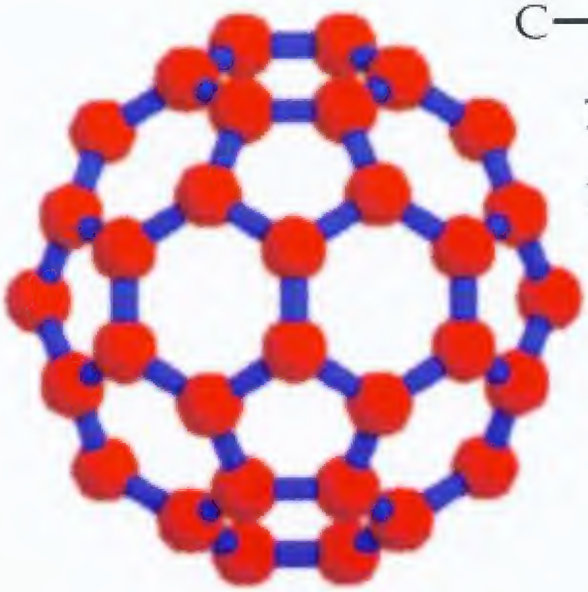
* Bednorz and Müller were awarded the physics Nobel prize for this discovery in 1987.

Fullerenes

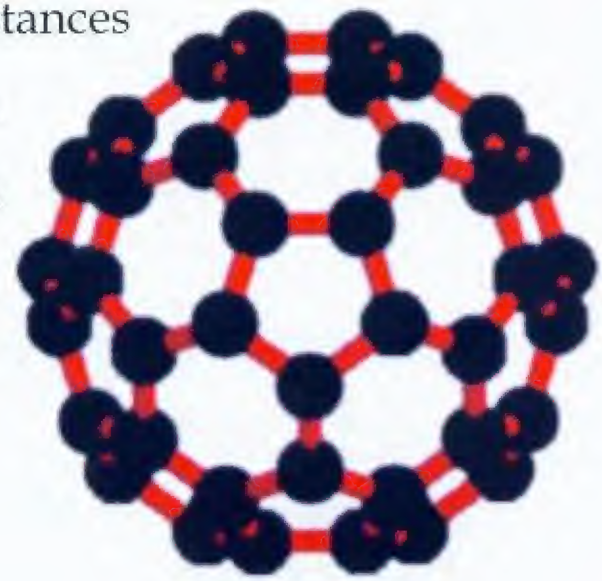
C— C distances

1.40 Å

1.45 Å



C_{60}



C_{70}

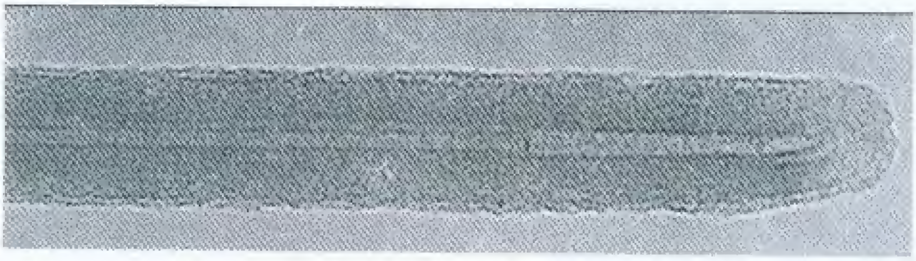
contain 6 - membered rings & 5 - membered rings

Discovered, 1985 (Kroto, Smalley et al.)

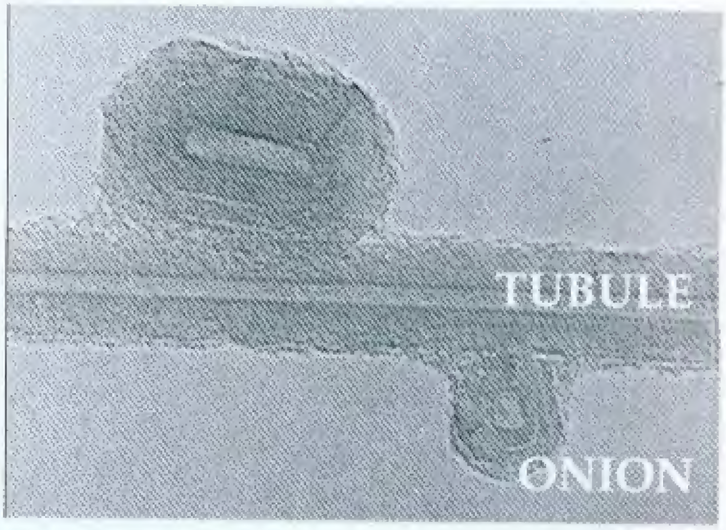
Prepared in the laboratory, 1990 (Kratschmer et al)

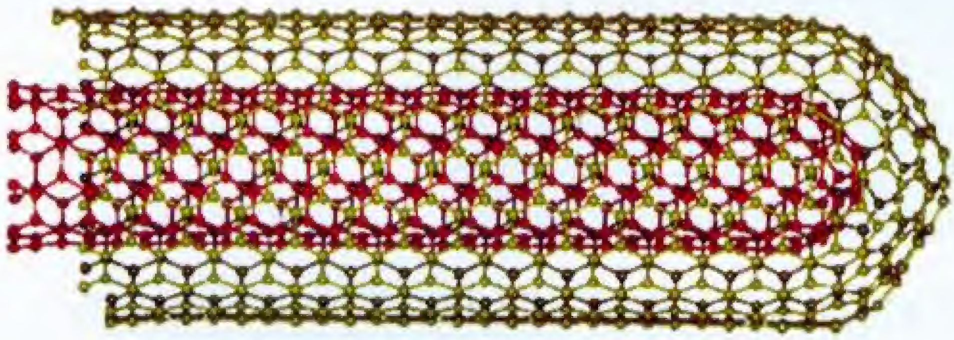
Nobel Prize to Curl, Kroto and Smalley (1996)

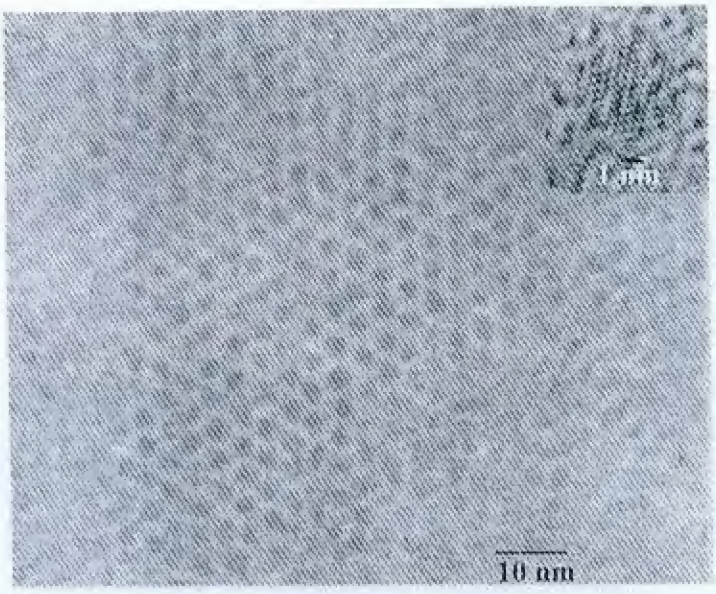
Carbon nanotubes



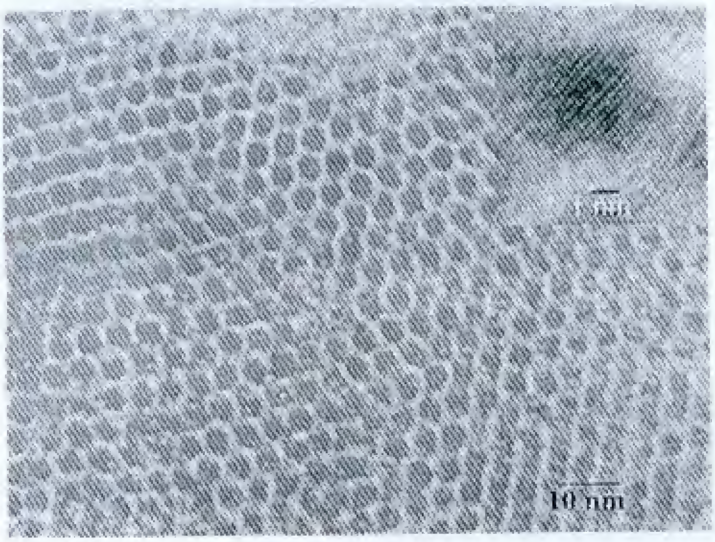
Discovered first by Endo 1976
Properly described by Iijima 1991







561 atoms in each particle (2.5 nm diameter)



1415 atoms in each particle (3.2 nm diameter)

2-D Crystalline array of metal nanocrystals

13.0 BEYOND THE MOLECULAR FRONTIER

Post 2000, there has been a change as to how one views chemistry!

Challenges for chemical sciences in the 21st century

The National Academy of Sciences
Washington, D.C., USA
2003

Chemistry!

new synthesis (new substances)

self-assembly

complex chemistry

(earth, sea, atmosphere......)

Chemistry - life

- Living systems
- Therapies
- Optimization as in biological systems.

Major areas of chemistry today

- Synthesis
- Chemical & physical transformations of matter
- Imaging structures
- Chemical theory & computer modeling
- Interface with biology & medicine
- Materials by design
- Atmosphere & environment
- Energy

Materials by design

- complex structures
- novel design
- new properties
- improved materials
- nanoscale
- biological function

Chemical theory and computational chemistry

- new computer methods
- large scale simulations
- simulation *vs* experiment
- theory *vs* experiment
- new algorithms

Nanochemistry

Zero - dimensional nanomaterials (Quantum dots)

One - dimensional nanomaterials (wires, nanotubes)

Two - dimensional nanomaterials (films, graphene)

Applications of nanomaterials

- Electronics
- Energy
- Biology, Health
- Chemical & Textile industries

Hybrid materials

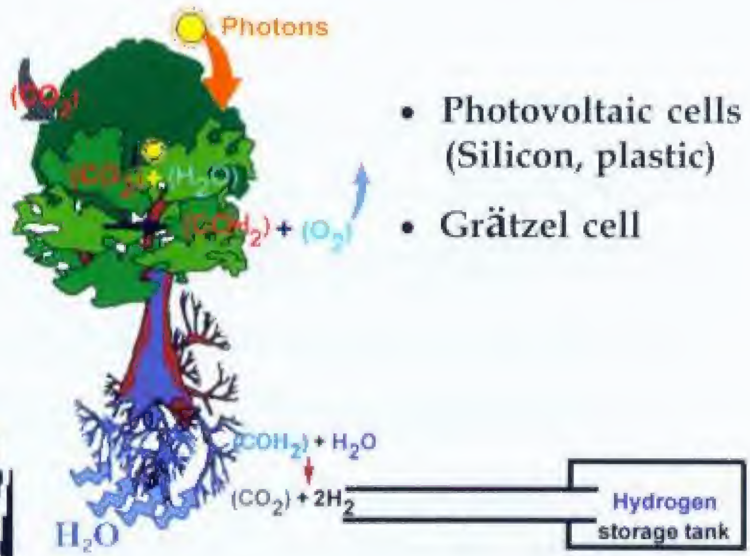
Inorganic	**Organic**
Magnetic materials	Magnetic materials
Ferroelectrics	Ferroelectrics
Superconductors	Superconductors
Non-linear optical materials ......etc	Non-linear optical materials......etc

There is room in the middle!

Energy and environment

Chemical approaches to energy (storage, generation)

- Hydrogen
- Solar
- Fuel Cells
- Batteries (Li etc)
- Supercapacitors



- **Photovoltaic cells (Silicon, plastic)**
- **Grätzel cell**

Hydrogen Fuel Cell

$$H_2 + 1/2\, O_2 \longrightarrow H_2O + \text{Energy}$$

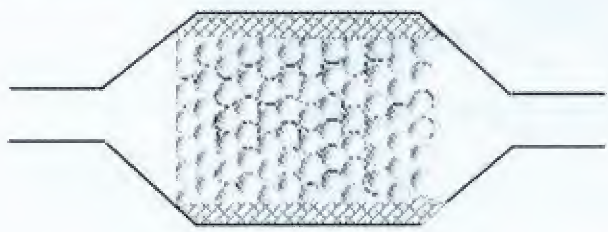
How to make H_2 easily, and how to store it in a solid!

Atmospheric chemistry

The cause of the ozone hole was discovered through chemical research.

Climate change, monsoons and other aspects of our environment and atmosphere can be understood and modeled only on the basis of the chemical processes involved. It is important to pursue dynamics of chemical reactions involved in causing pollution, brown clouds and global warming.

Better autoexhaust catalysts



Catalysis

- Haber's synthesis of ammonia is the greatest example of a catalytic reaction.
- Heterogeneous catalysis is employed for the synthesis of important chemicals. Modern petrochemical industry has depended highly on advances in catalysis.
- Homogeneous catalysis is of interest as well. Chemists make use of biological catalysis and the lessons learnt from it in carrying out chemical transformations.
- There are many challenges that we face in catalysis. Some of them are closely connected to environmental problems.

  e.g., We need inexpensive autoexhaust catalysts which do not use noble metals. We need catalysts to convert CO_2 or carbonates to organic molecules.

Our industry

The greatest success in Indian industry has been in chemical and pharmaceutical sectors.

Our petrochemical industry has been producing polymers and fuels in large quantities.

Our pharmaceutical industry has excelled in innovation and leadership. Indian research and development in this sector has brought great dividends.

It will be wonderful if we can discover new molecules to combat some of the dreaded diseases. A few such molecules would not only make the industry rich but also make us proud.

Chemistry forms a major part of materials industry as well. A high proportion of nanotechnology is chemistry.

14.0 IN CLOSING

Chemistry is the

queen

and

Servant

of biology

as well as of

materials

Science.

The devil may write chemical text books because every few years, the whole thing changes

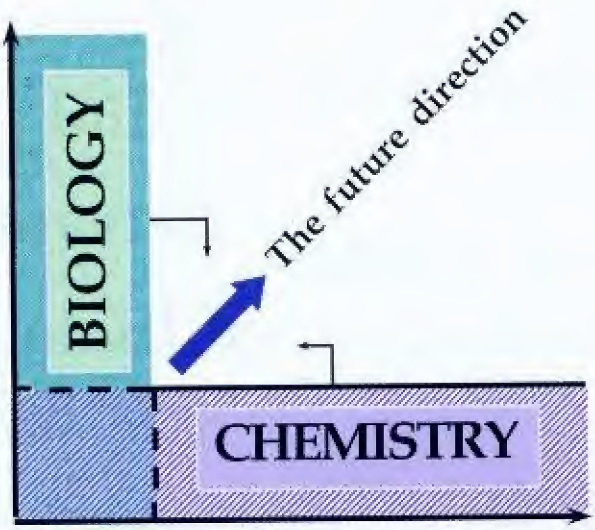
- J. J. Berzelius

(1779-1848)

Complexity versus Diversity

Complexity

Classes of molecules
& systems
(individually complex,
yet commonality)



Diversity / Breadth

More & more systems,
compounds,

- Scope of chemistry is unlimited
- There are surprises, all the time
- The way we do chemistry, and the chemistry we do, are both changing.
- Chemistry builds bridges in science.

PHYSICS ⟷ CHEMISTRY ⟷ BIOLOGY

Chemists do not make war.

They find ways to alleviate human suffering.

Chemists do not cause pollution.

They improve the quality of life.

About the author

C. N. R. Rao is the National Research Professor, Linus Pauling Research Professor at the Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR) and honorary professor at the Indian Institute of Science (IISc). He is an author of 1400 research papers and has written or edited 43 books dealing with spectroscopy, solid state and materials chemistry, superconductivity, nanomaterials and such topics. Some of his books are meant for school and college students. He has received 48 honorary doctorate degrees from Indian and foreign universities. He is a member of most of the major science academies including the Royal Society (London) and U. S. National Academy of Sciences, as well as French, Japan and Pontifical Academies.

C. N. R. Rao has received numerous prizes and medals of which mention must be made of the Marlow medal of the Faraday Society (1967), Bhatnagar Prize (1968), Einstein gold medal of UNESCO (1996), Hughes medal (2000) as well as the Royal medal (2009) of the Royal Society (London). He is the first recipient of the India Science Award of the Government of India (2005) and received the Dan David Prize for science in the future dimension in 2005 for his work on advanced materials. The August-Wilhelm-von-Hoffmann Medal (2010) has just been conferred by the German Chemical Society.

He was conferred the Order of Scientific Merit (Grand-Cross) in 2002 by the President of Brazil, and the Chevalier de la Légion d'Honneur by the President of France in 2005. He has been a distinguished professor at the Universities of Oxford, Cambridge and California. He was President of the International Union of Pure and Applied Chemistry.